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Thermal Conductivity and Heat Capacity of Synthetic Fuel Components[1]

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As part of a group contribution study on the liquid thermal conductivity of synthetic fuel components, experiments were performed to study the effects of dimethyl- and ethyl-group additions to cyclohexane. A transient hot-wire apparatus was used to measure the thermal conductivity of these three fluids between ambient pressure and 10.4 MPa over a temperature range of 300 to 460 K. Thermal conductivities measured with this instrument have been assigned an accuracy of ±2% based upon a standard deviation comparison with a toluene standard established by Nieto de Castro et al. (1986). The thermal conductivities and excess thermal conductivities of the naphthenes investigated have been successfully linearized by plotting the data versus reduced density exponentiated to the power of five. By using data previously reported by Perkins (1983) and Li et al. (1984), this linear reduced density method is demonstrated for methyl, dimethyl, and ethyl additions to cyclohexane, as well as methyl and dimethyl additions to benzene. The naphthenes have been shown to have similar intercepts, with slope changes dependent upon the functional group attached to cyclohexane. The aromatics have a less pronounced slope change with additional functional groups attached to the benzene base. This instrument was also used to determine heat capacities, via the thermal diffusivity, to within ±10%.

KEY WORDS: aromatics; heat capacity; naphthenes; transient hot-wire method; thermal conductivity; toluene.

1. INTRODUCTION

Oil shale and coal liquefaction products will eventually play a large role in supplying this nation's energy demand. In the event that another oil crisis

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should develop, the partial transition to alternate fuels must be as swift as possible. To accomplish this goal, an accurate thermophysical data base must be upgraded at the present time [1]. The goal of the present work is to contribute to this data base.

A survey of the existing thermal conductivity data shows that a good portion is 15 or more years old. Unfortunately, much of the older data were measured by methods that were plagued with convection and radiation. These effects, unless corrected, cause the data to be artificially high (as much as 20%, or more in some instances). For example, the accepted value for the thermal conductivity of toluene at 20°C has decreased from approximately 150 $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$ in the 1920s to the current value of 131.1 $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$ [2]. High thermal conductivities lead to overestimated heat transfer coefficients, which in turn, lead to underestimated heat transfer surface areas. This underestimation will undoubtedly diminish a process design's safety factor or rated optimal efficiency.

With the exception of the many possible heteromolecules that are common components in coal liquefaction, four common types of molecules encountered in various stages of processing oil and coal liquids are paraffins (alkanes and branched alkanes), olefins (alkenes and cycloalkenes), naphthenes (cycloalkanes), and aromatics.

Of the four classes of molecules mentioned, the paraffinic group has the most reported thermophysical data. The majority of the olefin thermal conductivity data has been taken at low temperatures (less than 50°C) due to the thermal instability of this molecular type. Problems with obtaining the desired chemical purity of the common cycloalkenes eliminated them from further study in this work. Any measurement of cycloalkenes at higher temperatures and pressures runs the risk of some degree of polymerization.

Some of the most common molecular base structures encountered in coal liquefaction and crude processing are six-member rings. The six-member naphthene ring is cyclohexane, and the six-member aromatic ring is benzene. Petroleum crudes from certain areas (California in particular) are rich in cycloalkanes (naphthenes) [3]. These are in turn, converted to high-octane aromatics by catalytic reforming.

The fluids chosen for this work were cyclohexane, *cis*-1,2-dimethylcyclohexane, and ethylcyclohexane. Data for these compounds were used along with methylcyclohexane data by Perkins [4] to show the effect on the thermal conductivity associated with the addition of methyl, dimethyl, and ethyl groups to cyclohexane. A similar analysis was made for methyl and dimethyl additions to benzene using reported experimental data by Perkins [4] and Li et al. [5].

2. EXPERIMENTAL APPARATUS

The instrument used to measure the thermal conductivity was a single-wire transient hot-wire apparatus described previously [6, 7]. The thermal conductivity data measured with this equipment were assigned an uncertainty of ±2% based upon a standard deviation comparison with the toluene thermal conductivity standard established by Nieto de Castro et al. [2].

The system was also used to measure the density within 2% by measuring volumetric changes in a closed system from a condition of known density [8]. A calibrated piston pressure generator is used to measure any change in the system volume. A mass balance can be applied to determine the fluid density at temperatures and pressures other than ambient. The governing mass balance equations are given by Voss [9]. All densities reported in this work compared within 1% with those calculated using a corresponding-states computer program (TRAPP) which is estimated at having an average absolute error of 8% [10].

Thermal diffusivities were also determined to within ±7% using the zero-time intercept of a ΔT vs $\ln(t)$ plot, where ΔT is the temperature rise of the transient hot wire in K and t is the experimental time in s. By applying the definition of the thermal diffusivity, the heat capacity was determined as

$$C_{\mathrm{p}} = \frac{\lambda}{\rho a} \tag{1}$$

where λ is the thermal conductivity, a is the thermal diffusivity, and ρ is the fluid density.

Due to the high degree of uncertainty associated with a thermal diffusivity determination, the heat capacity determination has been assigned an uncertainty of ±10%. This accuracy cannot compete with calorimetric data but can be used for process design purposes if no other data are available for the fluid or conditions of interest. All pressures measured during this work were determined within 0.015 MPa and temperatures within 1°C.

3. RESULTS

Tables I through III show the experimental results for the three naphtenes investigated over the course of this work. The ideal-gas thermal conductivity (λ^0) has been estimated using a corresponding-states computer program (TRAPP) [10] which has an average absolute error of 8%. The thermal conductivity of *cis*-1,2-dimethylcyclohexane is plotted versus

Table I. Experimental Results for Cyclohexane

T (K)	P (MPA)	ρ ($g \cdot cm^{-3}$)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	λ^0 ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\lambda - \lambda^0)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	C_p ($J \cdot g^{-1} \cdot K^{-1}$)
326.5	0.4	0.749	108.3	13.6	94.7	1.71
326.5	3.5	0.753	110.0	13.6	96.4	1.72
326.5	7.0	0.756	111.1	13.6	97.5	1.73
326.5	10.4	0.760	113.1	13.6	99.5	1.75
341.4	0.4	0.734	103.8	14.9	88.9	1.76
341.4	3.5	0.738	105.2	14.9	90.3	1.76
341.4	7.0	0.742	106.8	14.9	91.9	1.77
341.4	10.4	0.746	108.8	14.9	93.9	1.79
355.7	0.4	0.719	99.5	16.3	83.2	1.80
355.7	3.5	0.724	102.0	16.3	85.7	1.83
355.7	7.0	0.729	103.8	16.3	87.5	1.84
355.7	10.4	0.734	105.5	16.3	89.2	1.85
375.6	3.5	0.705	95.8	18.3	77.5	1.88
375.6	7.0	0.710	97.9	18.3	79.6	1.90
375.6	10.4	0.716	100.2	18.3	81.9	1.93
393.0	3.5	0.687	90.9	20.1	70.8	1.94
393.0	7.0	0.693	93.2	20.1	73.1	1.97
393.0	10.4	0.699	95.0	20.1	74.9	1.98
422.2	3.5	0.657	85.2	23.4	61.8	2.11
422.2	7.0	0.664	87.8	23.4	64.4	2.14
422.2	10.4	0.671	89.1	23.4	65.7	2.15
450.0	3.5	0.624	79.8	26.7	53.1	2.31
450.0	7.0	0.635	81.5	26.7	54.8	2.31
450.0	10.4	0.644	83.3	26.7	56.6	2.32

Table II. Experimental Results for *cis*-1,2-Dimethylcyclohexane

T (K)	P (MPa)	ρ ($g \cdot cm^{-3}$)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	λ^0 ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\lambda - \lambda^0)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	C_p ($J \cdot g^{-1} \cdot K^{-1}$)
325.2	0.4	0.775	100.9	12.1	88.8	1.55
325.2	3.5	0.778	101.7	12.1	89.6	1.55
325.2	7.0	0.781	102.9	12.1	90.8	1.55
325.2	9.7	0.784	103.8	12.1	91.7	1.56
340.6	0.4	0.763	97.4	13.3	84.1	1.58
340.6	3.5	0.766	98.5	13.3	85.2	1.58
340.6	7.0	0.770	99.4	13.3	86.1	1.59
340.6	9.7	0.773	100.3	13.3	87.0	1.59
359.1	0.4	0.748	93.6	14.8	78.8	1.64
359.1	3.5	0.752	94.8	14.8	80.0	1.65
359.1	7.0	0.757	95.9	14.8	81.1	1.65
359.1	9.7	0.760	96.8	14.8	82.0	1.65
380.2	3.5	0.735	90.8	16.7	74.1	1.73
380.2	7.0	0.740	92.0	16.7	75.3	1.74
380.2	9.7	0.744	93.1	16.7	76.4	1.74
406.0	3.5	0.715	86.1	19.1	67.0	1.85
406.0	7.0	0.721	87.3	19.1	68.2	1.85
406.0	9.7	0.725	88.4	19.1	69.3	1.86
433.3	7.0	0.699	83.0	21.8	61.2	2.03
433.3	9.7	0.704	84.0	21.8	62.2	2.03
461.2	9.7	0.681	80.7	24.8	55.9	2.21

Table III. Experimental Results for Ethylcyclohexane

T (K)	P (MPa)	ρ ($g \cdot cm^{-3}$)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	λ^0 ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\lambda - \lambda^0)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	C_p ($J \cdot g^{-1} \cdot K^{-1}$)
327.1	0.4	0.769	101.2	12.4	88.8	1.56
327.1	3.5	0.772	102.7	12.4	90.3	1.58
327.1	7.0	0.776	104.0	12.4	91.6	1.59
327.1	9.7	0.778	104.9	12.4	92.5	1.59
341.8	0.4	0.757	98.1	13.6	84.5	1.61
341.8	3.5	0.761	99.5	13.6	85.9	1.63
341.8	7.0	0.764	100.8	13.6	87.2	1.64
341.8	9.7	0.767	102.0	13.6	88.4	1.65
357.3	0.4	0.745	94.6	14.9	79.7	1.67
357.3	3.5	0.749	96.1	14.9	81.2	1.68
357.3	7.0	0.753	97.5	14.9	82.6	1.69
357.3	9.7	0.756	98.6	14.9	83.7	1.70
372.1	0.4	0.733	91.7	16.2	75.5	1.72
372.1	3.5	0.737	93.0	16.2	76.8	1.74
372.1	7.0	0.741	94.5	16.2	78.3	1.75
372.1	9.7	0.745	95.5	16.2	79.3	1.76
401.3	3.5	0.714	87.4	18.9	68.5	1.86
401.3	7.0	0.720	89.0	18.9	70.1	1.87
401.3	9.7	0.724	90.4	18.9	71.5	1.88
424.1	3.5	0.694	83.9	21.1	62.8	1.98
424.1	7.0	0.701	85.4	21.1	64.3	1.99
424.1	9.7	0.706	86.6	21.1	65.5	2.00
440.9	7.0	0.687	83.0	22.9	60.1	2.11
440.9	9.7	0.692	84.0	22.9	61.1	2.11

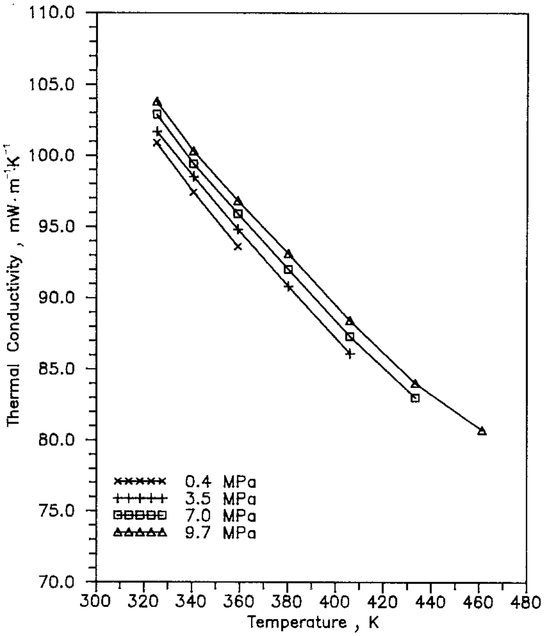

Fig. 1. Thermal conductivity of cis-1,2-dimethylcyclohexane.

temperature for the isobars of 0.4, 3.5, 7.0, and 9.7 MPa in Fig. 1. The thermal conductivity plotted by this method yields a distinct curve for each isobar. Figure 1 is typical of the thermal conductivity data plots for the fluids investigated in this work.

4. REDUCED DENSITY METHOD

It was shown by Voss [9] that the experimentally measured naphthene thermal conductivity data were linearized by plotting them bersus reduced density to the power of five (ρ_r^5), where the reduced density is the fluid density divided by the fluid critical density. This method linearized the liquid thermal conductivity data over the temperature and pressure ranges investigated to reduced densities as low as 2.0 and to pressures as high as 10.4 MPa. The naphthene thermal conductivities have been put into a form of

$$\lambda = a\rho_r^5 + c \tag{2}$$

where λ is the experimentally measured liquid thermal conductivity. For this equation, λ as well as a and c have units of $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$. It was

Table IV. Naphthene Coefficients for Eq. (2)

Compound and source of data	a	c
Cyclohexane [8]	0.308	60.0
Methylcyclohexane [4]	0.215	61.9
cis-1,2 Dimethylcyclohexane [8]	0.149	56.5
Ethylcyclohexane [8]	0.155	56.9

also shown that reduced density exponents between 4.0 and 6.0 linearized the data. The exponent of 5.0 was used to be consistent throughout this work. The naphthene coefficients for Eq. (2) are given in Table IV.

From a corresponding-states standpoint, the thermal conductivity can be divided into several parts and correlated as a function of the *PVT* properties of a system [11]. In its simplest form, the excess thermal conductivity is given as

$$\lambda - \lambda^0 = f(\rho) \tag{3}$$

The ideal-gas thermal conductivity is subtracted since it is a function of temperature only [12].

Naphthene excess thermal conductivities have been determined using the following data sources: cyclohexane experimental data by Voss [9] and Li et al. [5], methylcyclohexane data by Perkins [4], and cis-1,2-dimethylcyclohexane and ethylcyclohexane data by Voss [9]. The naphthene excess thermal conductivities are plotted versus ρ_r^5 in Fig. 2. The excess thermal conductivities for the naphthenes are linearized for each fluid and can be easily put into the form

$$\lambda - \lambda^0 = m\rho_r^5 + b \tag{4}$$

The naphthene coefficients for Eq. (4) are given in Table V. The units of λ, λ^0, m, and b are all $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$. The data in Table V and Fig. 2 indicate that the naphthenes investigated have been linearized with slopes changing as a function of the group attached to the cyclohexane base.

We believe that the slope changes associated with the various group additions (in Fig. 2) are due to an increase in the molecular internal degrees of freedom. For a given energy input to an individual molecule, increased internal degrees of freedom give the molecule greater ability to store heat within itself (in the form of rotational and vibrational energies), decreasing the energy available as translational energy, since energy is conserved. Therefore, a decrease in the translational energy will decrease the amount of energy transferred to neighboring molecules resulting in a

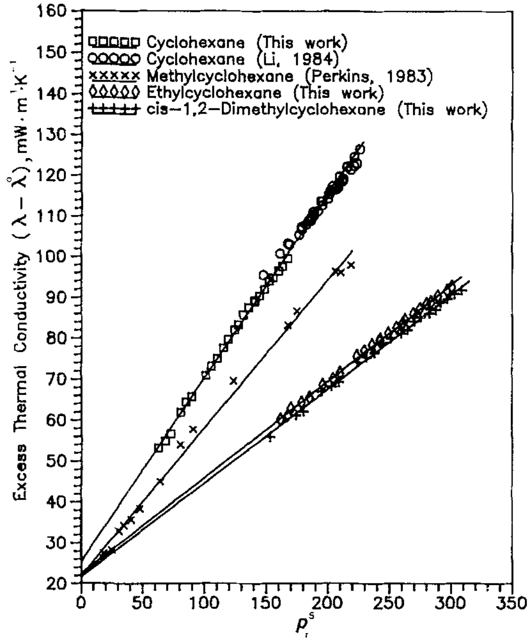

Fig. 2. Naphthene excess thermal conductivities plotted by the reduced-density method.

decrease in the thermal conductivity. This result will be amplified as the density is increased since the number of neighboring molecules that can be affected increases.

This method has been extended to aromatics using experimental benzene data reported by Li et al. [5], toluene and *m*-xylene data reported by Perkins [4], and predicted densities and ideal-gas thermal conductivities using TRAPP [10]. The aromatic excess thermal conductivities, plotted versus ρ_r^5 in Fig. 3 are also linearized by this method. The aromatic coefficients for Eq. (4) are given in Table VI. Unlike the naphthenes, the slopes

Table V. Naphthene Coefficients for Eq. (4)

Compound and source of data	*m*	*b*
Cyclohexane [5, 8]	0.441	26.6
Methylcyclohexane [4]	0.362	21.8
cis-1,2 Dimethylcyclohexane [8]	0.230	21.6
Ethylcyclohexane [8]	0.235	22.4

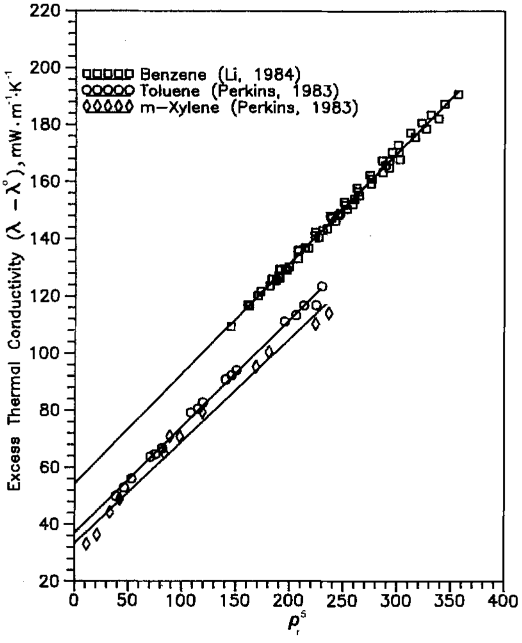

Fig. 3. Aromatic excess thermal conductivities plotted by the reduced-density method.

of aromatics do not change significantly with additional groups attached to the benzene ring. The intercepts also vary between benzene and the others. We believe that the small aromatic slope change with functional-group additions is due to the fact that the changes in the molecular internal degrees of freedom is much smaller with functional-group additions to an aromatic base than with an equivalent addition to a naphthene base. The aromatic coefficients for Eq. (2) are also given in Table VII. Benzene data by Li et al. [5] are not included in Table VII since Eq. (2) fails to linearize the thermal conductivity data above 10 15 MPa.

Overall, this method of reducing the data has been shown to be very consistent within experimental errors for the naphthenes and aromatics

Table VI. Aromatic Coefficients for Eq. (4)

Compound and source of data	m	b
Benzene [5]	0.386	54.1
Toluene [4]	0.377	36.8
m-Xylene [4]	0.360	33.1

Table VII. Aromatic Coefficients for Eq. (2)

Compound and source of data	*a*	*c*
Toluene [4]	0.264	70.8
m-Xylene [4]	0.241	70.2

investigated. It effectively linearizes the thermal conductivity data for temperatures between room temperature and near the critical point as well as for pressures between ambient and 0.33 GPa.

5. CONCLUSIONS AND RECOMMENDATIONS

A method has been presented which has been demonstrated to linearize both the excess and the experimental thermal conductivity data for the naphthenes and aromatics investigated over a significant portion of the entire liquid region within experimental errors. The extension of this method to other families of molecules to propose a correlation is a promising subject for further research.

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